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| (21) International Application Number: PCT/US87/02278 (22) International Filing Date: 3 September 1987 (03.09.87) (31) Priority Application Numbers: 903,130 905,135 (32) Priority Dates: 3 September 1986 (03.09.86) 9 September 1986 (09.09.86) (33) Priority Country: US (60) Parent Applications or Grants (63) Related by Continuation US 903,130 (CIP) Filed on 3 September 1986 (03.09.86) US 905,135 (CIP) Filed on 9 September 1986 (09.09.86) (71) Applicant (for all designated States except US): BURLINGTON INDUSTRIES, INC. [US/US]; 3330 West Friendly Avenue, Greensboro, NC 27420 (US). | | (72) Inventors; and (75) Inventors/Applicants (for US only) : TOWERY, Donald, R. [US/US]; 6303 Hagan Stone Park Road, Pleasant Garden, NC 27313 (US). HILL, Berlie, R. [US/US]; Route 1, Box 530, Cana, VA 24317 (US). WATSON, Thomas, F. [US/US]; 3214 Fontana Drive, Greensboro, NC 27406 (US). TRIPLETT, Benny, L. [US/US]; 2316 Corlford Road, Pleasant Garden, NC 27313 (US). (74) Agents: CRAWFORD, Arthur, R. et al.; Nixon & Vanderhye, 2000 North 15th Street, Suite 409, Arlington, VA 22201 (US). (81) Designated States: AT (European patent), AU, BB, BE (European patent), BG, BJ (OAPI patent), BR, CF (OAPI patent), CG (OAPI patent), CH (European patent), CM (OAPI patent), DE (European patent), DK, FI, FR (European patent), GA (OAPI patent), GB (European patent), HU, IT (European patent), JP, KP, KR, LK, LU (European patent), MC, MG, ML (OAPI patent), MR (OAPI patent), MW, NL (European patent), NO, RO, SD, SE (European patent), SN (OAPI patent), SU, TD (OAPI patent), TG (OAPI patent), US, US. Published <i>With international search report</i> <i>With amended claims .</i> Date of publication of the amended claims: 7 April 1988 (07.04.88) |
| (54) Title: MICROPOROUS COATINGS (57) Abstract Water-vapor-permeable yet waterproof coated fabrics are prepared by applying a polyurethane resin solvent solution to a base fabric then immersing the coating to coagulate the resin leaving a thin, microporous coating on the fabric. An acrylic acid thickener system is included in the resin solution to provide a microporous coating having moisture vapor transmission rates of at least 600 g/m ² /24 hours and hydrostatic pressure resistance of at least 69 kPa. The resin solution may contain a bioactive silyl quaternary ammonium compound to impart laundry-durable antimicrobial properties to the coating and/or a hindered amine ultraviolet stabilizer to protect the coating from degradation caused by ultraviolet light and/or a flame retardant to render the coated fabric resistant to flame. | | |

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AMENDED CLAIMS

[received by the International Bureau on 7 March 1988 (07.03.88);
original claims 9 and 10 replaced by amended claim 9; claims 11-17 renumbered as
claims 10-16 wherein claim 16 is amended (3 pages)]

7. A waterproof, water-vapor-permeable antimicrobial coated fabric resistant to the spread of mildew, produced by the process of claim 5.

8. A urethane-coated fabric with durable antimicrobial properties, a moisture-vapor transmission of at least $800\text{gm/m}^2/24$ hours, and a hydrostatic pressure resistance of at least 69 kPa.

9. A process of protecting a waterproof, water-vapor-permeable, coated fabric from ultraviolet light degradation, the coated fabric having a microporous polyurethane layer thereon formed by the wet coagulation method, said process comprising applying a water-miscible, polar organic solvent coating solution of an aromatic urethane elastomer to a base fabric, immersing the thus-coated base fabric into an aqueous coagulation bath to extract the solvent from the polymer solution leaving a porous aromatic urethane matrix adhered to the base fabric, then washing and drying the coated fabric, wherein the polyurethane elastomer solution contains an ultraviolet light protecting amount of hindered amine ultraviolet light stabilizer sufficient to provide effective protection against ultraviolet light for 20 hours in AATCC Test Method 16A-1982.

10. The process of claim 9 in which from about 0.1 to about 1.0 weight percent of the ultraviolet light stabilizer is present in the coating solution.

11. The process of claim 10 in which the amount

of ultraviolet light stabilizer is in the range of from 0.1% to about 0.5%.

12. The process of claim 9 in which the ultraviolet light stabilizer is bis(1,2,2,6,6-pentamethyl-4-peperidinyl)sebacate.

13. A waterproof, water-vapor-permeable ultraviolet light-resistant coated fabric produced by the process of claim 9.

14. A coated fabric having a thin, microporous aromatic urethane coating thereon resistant to degradation from ultraviolet light for at least 20 hours according to AATCC Test Method 16A-1982.

15. A coated fabric with a thin, microporous aromatic urethane coating thereon having a moisture-vapor transmission of at least $800\text{g/m}^2/24$ hours, a hydrostatic pressure resistance of at least 69 kPa and resistant to ultraviolet light for at least 20 hours according to AATCC Test Method 16A-1982.

16. A process of flame retardant treating a water-proof, water-vapor-permeable, coated fabric having a microporous polyurethane layer thereon formed by the wet coagulation method, said process comprising applying a water-miscible, polar organic solvent coating solution of an aromatic urethane elastomer to a base fabric, immersing the thus-coated base fabric into an aqueous coagulation bath to extract the solvent from the polymer solution

leaving a porous aromatic urethane matrix adhered to the base fabric, then washing and drying the coated fabric, wherein the polyurethane elastomer solution contains a flame-retarding amount of a mixture of antimony oxide and hexabromocyclododecane as a flame retardant.

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| (54) Title: MICROPOROUS COATINGS | | | |
| (57) Abstract <p>Water-vapor-permeable yet waterproof coated fabrics are prepared by applying a polyurethane resin solvent solution to a base fabric then immersing the coating to coagulate the resin leaving a thin, microporous coating on the fabric. An acrylic acid thickener system is included in the resin solution to provide a microporous coating having moisture vapor transmission rates of at least 600 g/m²/24 hours and hydrostatic pressure resistance of at least 69 kPa. The resin solution may contain a bioactive silyl quaternary ammonium compound to impart laundry-durable antimicrobial properties to the coating and/or a hindered amine ultraviolet stabilizer to protect the coating from degradation caused by ultraviolet light and/or a flame retardant to render the coated fabric resistant to flame.</p> | | | |

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1.

MICROPOROUS COATINGS

TECHNICAL FIELD

This invention relates to an improved resin-containing coating solution which, when applied to a fabric substrate and processed to coagulate the resin, results in an improved, waterproof, microporous, moisture-vapor-permeable fabric. The invention also relates to protecting a moisture-permeable, waterproof, coated fabric from ultraviolet light deterioration as manifested by yellowing, loss or change of color, or loss of desirable mechanical properties. The coating solution may further include antimicrobial agents, ultraviolet light stabilizers and/or flame retardants which are also contained in and distributed throughout the cellular matrix of the finished microporous polymeric coating. The coated fabric retains good moisture permeability with durable waterproofness and other desirable properties (resistance to microbial attack and degradation caused by ultraviolet light and flame resistance, depending upon the components of the coating solution) that remain characteristic of the fabric even following multiple launderings. Procedures for making such fabrics are also described.

BACKGROUND

Coated fabrics suitable for use as activewear, rainwear and tentage function by blocking the pores of a woven, knitted or non-woven with a

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cohesive polymer film which acts as a physical barrier against wind, water, and in the case of protective workwear, aggressive chemicals, oils, and greases. This barrier or coating distinguishes polymer coatings from chemical finishes which merely coat the individual fibers of a fabric without blocking the pores, and repel fluids by surface tension effects. Microporous coated fabrics repel water from the outside yet allow perspiration and moisture vapor to escape from the inside. Moisture is transmitted through a tortuous physical pathway produced in the cellular film or coating resulting from the art-recognized wet coagulation process, as described in more detail below. Polymeric coatings have initially been based upon rubber or synthetic or fluorocarbon rubbers, and more recently, polyurethanes, acrylics, silicone elastomers and polyvinylchlorides.

Fashion and leisurewear, particularly rainwear, require that the coated material be attractive with good drape and handle, that it be water repellent, although not necessarily for prolonged use in heavy rain, and that the fabric retain these properties after dry cleaning or laundering.

There are several fabrics available that satisfy the conflicting requirements of waterproofness and breathability. One example is Entrant, which is a woven nylon fabric coated with a microporous polyurethane film formed by the so-called wet coagulation technique as described in U.S. Patent 4,429,000 to Toray Industries, Inc. Other polyurethane coated fabrics are described in U.S. Patent 3,360,394 to Griffin. In the wet coagulation

method, a thin, microporous polyurethane layer is formed on a base fabric by applying a coating solution of a polyurethane dissolved in a polar organic solvent that will solubilize the polyurethane yet is miscible with water. The polymer solution is applied to the fabric substrate by knife coating or the like, then immersed in a bath of water which selectively dissolves or mixes with the organic solvent, exchanges water for the polar solvent and causes the previously dissolved polyurethane to coagulate, leaving a thin, microporous coating having a cellular substrate on the fabric. Surface pores that result are generally one micron or less in diameter. Such pores are small enough to exclude water droplets and yet they provide a tortuous physical pathway from the base fabric to the coating surface, to allow water vapor to pass through the fabric. The coating is a thin polymeric (polyurethane) film.

Typical coating solutions contain a resin, usually a polyurethane elastomer, optionally a water repellent agent, a thickener, a surfactant, an ultraviolet light stabilizer and/or an antimicrobial and possibly other adjuvants, all dissolved in a water-miscible polar organic solvent such as dimethylformamide, N-methyl-2-pyrrolidone, dimethylacetamide or dimethylsulfoxide. The coagulating bath contains water with up to 20% by weight of the same or a compatible polar solvent. Coating viscosity must be carefully controlled to adjust penetration and interstitial strike-through, especially on loosely-woven and textured fabrics.

When coating textile fabric with a resinous

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material dissolved in a liquid medium, final distribution of the dried coating depends on several factors, including the coating method, fabric geometry, and coating viscosity. In many situations, coating viscosity is the variable most easily manipulated to control coating distribution. When dealing with true solution coatings, the solute molecular weight, solute concentration, and nature of the solvent have an influence on coating viscosity. However, optimum physical and handling properties of the coating are often obtained within specific ranges of molecular weight and polymer concentration. Application techniques can also severely limit solvent choices. With these practical operational constraints, a viscosity control additive is required. Traditional thickeners for such resin-containing solutions are natural and modified gums, solvent-interactive fillers, and high molecular weight synthetic polymers. The choice of thickening agent has traditionally been made on the basis of compatibility, coating performance requirements, and economics.

This invention provides a convenient, reliable thickener system exhibiting the required ease of processing without detracting from the desired physical properties of the finished product. Water-coagulable coatings for textiles must exhibit coagulation rates within relatively narrow limits to maintain reproducible fabric properties. Candidate thickeners must have little or no effect on coagulation rates. Disclosed is a thickener system that satisfies these various requirements.

Rain-soaked and badly soiled garments must be

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cleaned or at least dried before long term storage to prevent proliferation of airborne bacteria and fungal spores that find a warm, moist environment hospitable. Such organisms find the cellular structure of this type of fabric attractive and can attack certain synthetic polymers, causing degradation of the polymer, in some cases, or at least permanent discoloration. In susceptible polymer coatings, biodegradation may be initiated in microscopic cracks and can eventually lead to delamination of the coating from the fabric and consequent loss of waterproofness.

The cellular structure of this type of microporous coating is subject to contamination with body oils, particularly when used as an article of apparel, due to direct contact with the skin or indirect transmission through a lining fabric. Thus, the potential exists for the production of undesirable odors, mildew and even discoloration since all the ingredients needed are present, namely, moisture, heat, and a nutrient for bacteria. It is also known that organic polymers are subject to bacterial attack which can result in deterioration of the polymer. A real need exists for the prevention of these undesirable occurrences.

It is an object of this invention to impart to a microporous coated fabric the ability to prevent odor, discoloration, mildew, even discoloration due to bacterial growth. Furthermore, the coating retains its effectiveness even following repeated launderings.

Polymeric materials such as plastics, foams and fibers can be protected from deterioration caused by

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light by the use of either ultraviolet absorbers or ultraviolet light stabilizers. The deterioration is usually manifested by yellowing, loss or change of color, or loss of desirable mechanical properties. The commonly-used ultraviolet absorbers, or screening agents, are often benzophenone derivatives, such as 2-hydroxybenzophenone. These reagents absorb ultraviolet light and re-emit the energy at another less harmful wavelength, or as heat. They usually suffer some degradation in the process of saving the polymer from degradation.

Another object of this invention is to protect thin microporous polyurethane films from deterioration caused by ultraviolet light. Topical treatments are known to provide a modest degree of ultraviolet (UV) protection for coated fabrics. These treatments are water-based in nature, and must be applied as a final finish by a final pad, dry, cure procedure. With most coated fabrics, this approach works, but with a microporous coating having a cell structure of many voids or micropores generally one micron or smaller in diameter, the pores are small enough to exclude liquid water. The water-based UV-protective treatment therefore cannot penetrate the inner structure of the coating's matrix, leaving it unprotected, and it will yellow with aging or exposure to light.

Ultraviolet light stabilizers, of which hindered amine light stabilizers are a class, do not function by the typical mechanism of ultraviolet absorption, but rather interrupt the decomposition mechanism initiated by ultraviolet light. Tinuvin® 292 (registered trademark of Ciba-Geigy, Corp., Ardsley,

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New York), the stabilizer of choice in the present invention, is a hindered amine light stabilizer. Products providing effective protection against ultraviolet light for 20 hours in AATCC Test Method 16A-1982 are produced by this invention. This is the level of protection required by the U.S. marketplace for apparel end uses.

In addition to apparel uses, microporous coated fabrics are used for tentage and tarpaulins. Both uses demand waterproofness as a primary requirement. For both, a high water vapor transmission rate is very desirable, in order to prevent the accumulation of condensed moisture on the inner surface of the structure. Flame resistance, particularly in tents for both military and civilian use, is extremely important for articles constructed of microporous coated fabrics. As with the other components mentioned above, the flame-resistant coating must be durable to cleaning, usually laundering in water. Flame-resistant microporous coated fabrics are included within this invention.

Microporous coatings, as described above and elsewhere, are made by dissolving a polymer in a water-miscible solvent, then mechanically applying this solvent solution as a coating to a fabric. The thus-coated fabric is then immersed in a non-solvent, such as water. The microporous structure of the coating is completed when all the solvent has been displaced with the non-solvent, leaving a microporous layer on the base fabric.

Experience has made it clear that unprotected microporous coatings using aromatic polyester-based urethanes dissolved in N,N-dimethylformamide (DMF)

have a severe lightfastness problem, and will not meet the apparel industry standard of effective protection against ultraviolet light for 20 hours. Other highly desirable properties for particular applications and constructions, such as antimicrobial properties, and/or flame resistance may also be imparted to the microporous coatings by this invention.

DISCLOSURE OF THE INVENTION

Disclosed is a process for preparing a waterproof, water-vapor-permeable coated fabric that also preferably has antimicrobial properties, exhibits enhanced flame resistance and/or is protected from ultraviolet light degradation, while at the same time exhibiting good hydrostatic pressure resistance, formed in a rapid and reproducible manner by coagulation from a solvent solution of a polyurethane elastomer optionally containing a silyl quaternary ammonium bioactive material, a hindered amine ultraviolet light stabilizer and/or a flame retardant. The fabric is coated using the wet coagulation method in which a polymeric elastomer or mixture of polymeric elastomers is dissolved in a water-miscible polar organic solvent. The polymer solution to which from 0.01 to 10% by weight of a silyl quaternary ammonium bioactive material, from 0.1 to 1% by weight of the hindered amine ultraviolet light stabilizer and/or a flame-retarding amount of an effective flame retardant is added, calculated on the weight of the coating mix (preferably, all three are included), is coated onto a base fabric and then

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immersed in a coagulation water bath. The water extracts the polar organic solvent, which is itself water-miscible, from the coating, leaving a porous, spongy polyurethane matrix having the specified porosity and other properties, as well as the ultraviolet stabilizer bioactive material and flame retardant, when used, on the base fabric. Washing to remove any unextracted polar organic solvent and drying follow. Optionally, a water repellent fluorocarbon finish, or a second ultraviolet light stabilizer is later applied.

A convenient thickener system based on acrylic acid polymers that are compatible with the solvent/polyurethane system and soluble in the solvent may be used to control and adjust coating solution viscosity which, in turn, leads to thin, flexible polyurethane elastomer coatings having the optimum performance and customer acceptance properties. Most desirable coatings, when applied, are adjusted with the disclosed acrylic acid thickener system to have a viscosity in the range of at least 6 Pa·s, the required viscosity being higher, the more open the fabric structure. The acrylic acid polymer thickener system has a molecular weight in the range of about 450,000 to about 4,000,000 and is preferably based upon a combination of two different acrylic acid polymers having different molecular weights from within the designated range.

Preferred thickeners are the Carbopol resins, which are soluble in both water and in a water-miscible polar organic solvent such as dimethylformamide (DMF), and readily thicken upon addition of a base. Carbopol resins are manufactured

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by B.F. Goodrich, and are currently offered in six variations. These resins are acrylic acid polymers crosslinked with a polyalkenyl polyether and have an equivalent weight of 76. The resins most suited for thickening water-coagulable solvent coatings are: Carbopols 934, 940 and 941, with molecular weights of 3,000,000; 4,000,000; and 1,250,000, respectively. These resins dissolve in DMF to yield viscous, turbid solutions; apparently enough dimethylamine is present in DMF to partially neutralize the Carbopol resins. Carbopol 934 and 940 apparently are similar in structure, but the higher molecular weight of Carbopol 940 results in a higher viscosity. Carbopol 941 is different from the other two in that despite its lower molecular weight, it is an extremely efficient thickener at low concentrations and has a somewhat stringy rheology.

The supplier, B.F. Goodrich, recommends several secondary and tertiary amines for neutralization to obtain optimum performance with DMF. Of these, di-(2-ethylhexyl)amine was used at a much lower amount than that recommended by the manufacturer. B.F. Goodrich recommends 2.5 parts of di-(2-ethylhexyl)amine per part of Carbopol for neutralization; it was found that in DMF, only 0.5-.75 parts were necessary for maximum viscosity development.

In order to obtain the best balance of properties required, a 50/50 blend of Carbopol 941 (the more viscous but stringy polymer) and Carbopol 934 may be used; higher viscosity yields are obtained with blends of Carbopol 941 and 940.

The coating solutions of the present invention

are based upon urethane resins dissolved in a water-miscible, polar organic solvent. The type of urethane resin systems and components contained in the coating prior to or after coagulation may vary widely. Several such systems are disclosed in the art, for instance in U.S. 4,429,000 and elsewhere. The following is a preferred system. A preferred series of polyurethane resins are Textthane 620C and 420C available from Polymer Industries, a subsidiary of Morton Thiokol. They are aromatic polyester urethane resins, 620C characterized as a soft resin, and 420C as a firm resin; both resins are sold as dimethylformamide solutions.

The coating composition preferably also includes at least one surfactant to control the rate at which water exchanges with dimethylformamide in the wet coagulation process, which, in turn, affects the pore size of the urethane foam. Nonionic surfactants such as the Pluronic polyols, which are block copolymers of polyoxypropylene and polyoxymethylene, are suitable materials. The polyoxypropylene serves as hydrophobe and the polyoxyethylene as lipophobe. As with the acrylic acid thickener, a mixture of two of these nonionic surfactants gives the best results. Average molecular weight for the Pluronic L-35 is 1900, with polyoxypropylene equal to 50 weight percent. Pluronic F-68 has an average molecular weight of 8350 with the polyoxypropylene equal to 20 weight percent.

An amine is preferably added to neutralize the polyacrylic acid resin and several amines may be useful; however, best results were obtained with di(2-ethylhexyl)amine or with

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polyoxyethylene(15)octadecylamine (available as Ethomeen C/25 from Armac Chemicals Division of Akzo Chemie America). The water-miscible polar organic solvent of choice is N,N-dimethylformamide, commonly referred to as DMF (CAS registry number 68-12-2), although other compatible solvents such as dimethylacetamide or dimethylsulfoxide may be considered.

The base fabric may be woven, knit or nonwoven. Filament polyester was used in the examples that follow; however, nylon and polyester/cotton or nylon/cotton blends of various constructions may be used.

Typical urethane-based, water-coagulable coating compositions are as follows:

| | | |
|-------------------------------|---------|-------|
| Urethane resin(s) | Up to | 48% |
| Nonionic surfactant(S) | Up to | 8% |
| Water | Up to | 6% |
| Acrylic acid thickener | Up to | 1% |
| Amine | Up to | 0.15% |
| Antimicrobial* | 0.1 to | 10% |
| Ultraviolet light stabilizer* | 0.1 to | 1% |
| Flame retardant* | Up to | 15% |
| Water-miscible polar solvent | Balance | |

* When present

It will be understood that the coating composition may contain coating additives and adjuvants, such as a pigment or colorant, water repellent, antistat, etc. Alternatively, any or all of these and/or flame retardants, ultraviolet light

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protectants and antimicrobials may be applied to the fabric as an aftertreatment following formation of the microporous layer.

The quantities of each of these ingredients may be varied depending upon the result desired, for instance depending on the coating viscosity and total solids requirements. Each of the above-listed ingredients must be present in the minimum amount indicated or, if an optional ingredient, must be present in an amount of at least 0.1%. All parts and percentages herein are expressed by weight unless otherwise indicated. The minimum viscosity of the coating material, when applied to the base fabric is 0.5 Pa.s.

Performance requirements for urethane-coated fabrics will vary depending upon the application or end use to which the fabric is exposed. As a point of reference, and without particular limitation, a typical urethane-coated nylon taffeta for use in constructing sportswear will have the following minimum values:

| | |
|----------------------------------|--------|
| Moisture vapor transmission rate | |
| (g/m ² /24 hours) | 800 |
| Hydrostatic pressure resistance | 69 kPa |

The coating solutions are prepared and then applied to the fabric substrate according to the following procedure:

Preparing the Thickener in Liquid Form. The Carbopol acrylic acid-type resins are supplied as dry powders of a very low apparent density and are

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prone to dust and float around the working area. To minimize this inconvenience, it has been found convenient to prepare a stock solution in DMF. The Carbopol resin and DMF are pre-weighed separately and the Carbopol is slowly sifted into rapidly agitated DMF, with stirring continued until no gel structure is evident. At this point, the Carbopol resin is neutralized to achieve maximum viscosity. A stock solution so prepared appears to have extended shelf life.

In addition to the thickeners, surfactants and other ingredients required to produce the microporous coating characterizing this invention, other components, active in their own right and capable of imparting desirable, often essential, properties to specific applications and constructions, may be included in the coating composition. These additional functional components, upon coagulation, become entrapped in the cellular matrix of the microporous coating, are resistant to removal or solubilization by water and remain in the coating in quantities effective for the intended purpose even following multiple launderings. These functional components, described in detail below, may be selected for inclusion in the coating composition, depending upon the intended use of the resulting product.

Certain antimicrobial agents have the ability to chemically bond to fibers and retain their effectiveness over a long period of use. One of these antimicrobial agents is 3-(trimethoxysilyl)-propyloctadecyldimethylammonium chloride, produced by Dow Corning Corporation and marketed under the

name of DC-5700. Initially, a topical application of this material to a microporous coated fabric provided a durable, bacteriostatic product. This approach was tried with good results. However, since various types of fabrics that are coated require different amounts of coating to achieve desired properties, and in some cases this coating can be relatively thick, it was not known whether the topical treatment effectively permeated the entire coating. For these reasons it appeared that the most effective way to insure completeness of treatment with the antimicrobial agent would be to include it in the coating itself. Unfortunately, the improved bioactive compound is furnished by the supplier as a solution in methanol, which is not a solvent for polyurethane, the polymer used in many microporous coatings. Being a non-solvent, the methanol coagulated the polymer when the bioactive compound, with its methanol solvent, was added to the coating solution. However, it was found using the proper technique that the bioactive compound could be first dissolved in N,N-dimethylformamide (DMF), a solvent for polyurethanes, and then incorporated into the coating solution. By first solving this coagulation/addition problem, it was then possible to produce a coagulated, microporous coating having an antimicrobial agent throughout the entire cellular matrix which would give maximum protection against bacterial growth, coupled with maximum durability. The result is that not only is the coating protected from undesirable bacterial growth but the fabric, being in such close proximity to the now bacteriostatic coating, is also rendered

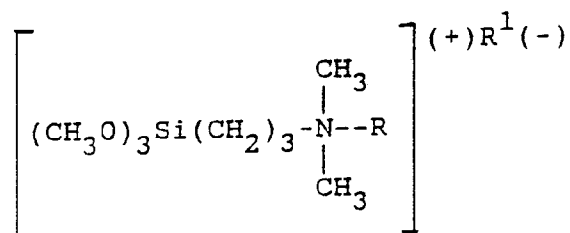
bacteriostatic. This finding does not preclude the possibilities in some cases of an additional treatment of the fabric itself either as a post-treatment finish or a pretreatment prior to coagulation, or treatment of the combined fabric and coating with the bioactive compound if a need arises. In fact, a treatment of coated fabric with the bioactive compound is effective; however, with the discovery of the ability to include the bioactive compound not merely on but in the coating a more complete and effective protection is provided.

An additional and unexpected benefit of the addition of the bioactive compound to the coating was that a softer product with better drape and hand was obtained as compared to the same coating applied to a fabric without the addition of the bioactive compound.

The coagulation process requires the water in the coagulation bath to exchange with the solvent in the coating solution, as explained above. Because methanol, as in the commercially available DC-5700, is completely water soluble, it was expected that this would influence the substantivity of the bioactive compound, i.e., that the bioactive compound would also be exchanged and removed with the coating solvent. Surprisingly, it has been discovered that the bioactive compound is actively bound to the coagulated microporous coating since the water coagulation bath following coating and coagulation, on analysis, did not reveal the presence of any bioactive compounds. This is substantiated by the results of multiple home

laundering; while some loss of the bioactive compound occurs, the coated fabric remains bioactive. Even after 10 machine washings, bacterial growth is prevented, as explained in more detail in the evidence below.

The preferred bioactive, antimicrobial component of the coating composition is a member of the class of silyl quaternary ammonium compounds. The preferred bioactive material is 3-(trimethoxysilyl)-propyloctadecyldimethylammonium chloride which is described in U.S. Patent No. 3,730,701. This class of suitable bioactive silyl quaternary ammonium compounds has the formula:



in which R is a C₁₁₋₂₂ alkyl group and R¹ is chlorine or bromine. The preferred silyl quaternary ammonium salt is 3-(trimethoxysilyl)-propyloctadecyldimethylammonium chloride and is available as a 42% active solids solution in methanol from Dow Corning Corporation of Midland, Michigan, U.S.A., under the designation DC-5700. This material is well accepted in commerce and has the necessary U.S. regulatory approvals, not only as a bacteriostatic textile treatment, but also as a bactericidal component for medical device/non-drug application.

When used, the amount of the silyl quaternary ammonium bioactive material will be within the following limits: the minimum amount is the quantity

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needed to achieve a specific minimum level of bioactivity, or to allow for process variations, if any, to maintain a specific predetermined level. The maximum amount will be limited by loss of substantivity on or in the coating as evidenced by excessive wash- or leach-out during laundering or in use, or otherwise, and is balanced by the cost of this relatively expensive component. Best results are obtained when the silyl quaternary ammonium salt is present in an amount of from 0.01 to 10% by weight, calculated on the weight in the coating mix, and preferably in the range of 0.08% and 4% by weight similarly calculated.

The mechanism of bacterial reduction is by activity of the antimicrobial in solution, and this means that the antimicrobial must leach out from the treated fabric to be effective. To be effective, leaching is required, and when leaching occurs, the durability of the treatment must be finite since, eventually, it will become depleted.

The ultraviolet screening agent used in the present invention is a hindered amine ultraviolet light stabilizer, preferably a bis(polyalkyl-4-piperidinyl) sebacate, and most preferably bis(1,2,2,6,6-pentamethyl-4-piperidinyl) sebacate. The amount of ultraviolet light stabilizer included in the aromatic urethane coating composition is at least sufficient to provide the degree of light protection required for the specific end use of the coated fabric although excessive quantities will be avoided for economic reasons. An amount of active material in the coating mixture ranging from 0.1% to about 1% will provide a degree of protection.

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sufficient to satisfy AATCC standard 16A-1982.

Following formation of the ultraviolet screening agent-containing microporous film, the fabric may be finished with a top coat of an additional quantity of the same or a compatible ultraviolet screening agent or with a pigment such as titanium dioxide to further enhance protection to degradation caused by ultraviolet light.

Flame retardants may be included in the coating composition when flame resistance is desired for the finished product. Suitable flame retardants, as exemplified below, are incorporated into the organic solvent-based coating composition and result in a uniform, tightly-bound flame retardant distributed throughout the urethane matrix. To be durable to cleaning, the flame retardant must be securely bound to the coating and, preferably, insoluble in the cleaning media yet soluble in the organic solvent of the coating composition. The amount of flame retardant included is at least sufficient to impart to the coated fabric a minimum resistance to flame (according to the relevant criteria) up to a limiting amount that causes the fabric to become stiff and brittle. Expense may also be a limiting factor and the solubility of the particular flame retardant or mixture of retardants in the organic solvent must also be considered. Illustrative flame retardants include hexabromocyclododecane, pentabromodiphenyl oxide, bis(tribromophenoxy) ethane; however, successful results will be obtained with other available materials.

The coating formulation is prepared as follows: the urethane resin or mixture of resins

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is preweighed into a container. Water, the polar organic solvent, usually DMF, the surfactant, and, optionally, the silyl quaternary ammonium salt bioactive material and/or the hindered amine-type ultraviolet light stabilizer and/or the flame retardant are preweighed into a separate container and mixed thoroughly. Other components of the type described above may be included. The water/solvent mixture is then added to the urethane under agitation. The optimum procedure for mixing of ingredients and order of mixing will be determined through a brief series of small-scale experiments, care being taken to avoid premature coagulation of the coating solution.

Once the coating solution is prepared, the urethane coating is applied to any textile substrate capable of supporting the liquid film by any conventional coating method appropriate for use in the wet coagulation method. The coated fabric is then dipped in a coagulation bath consisting of water, or water and an additive to alter or adjust coagulation, e.g., DMF, a surfactant, etc. During the coagulation step, the majority of DMF in the DMF/urethane film migrates into the coagulation bath and is replaced by water, generating a coherent, tenacious, microporous, spongy film on the fabric surface. After additional washing to remove any remaining DMF, the fabric is dried and optionally given an water repellant finish.

Performance Characteristics and Evaluations.

The following examples evaluate various coated fabrics as to moisture vapor transmission rate (MVTR) measured according to ASTM E96-80,

Procedure

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A; Mullen Hydrostatic Resistance (MH) measured according to ASTM D751-79; flame resistance measured by (U.S.) Federal Test Method Standard No. 191, Method 5903; and coating weight (CW) measured as grams of coating applied per square meter.

The invention will be further explained with reference to the following examples in which all parts and percentages are by weight unless otherwise indicated.

Example 1 and Comparative Example B

Coating mixture (A) was prepared by mixing a previously prepared (as described above) acrylic acid thickener solution in DMF with a mixture of urethane resins, nonionic surfactant and diluents; a similar formulation (B) was prepared but without the acrylic acid thickener and thus not according to the present invention. The formulations, expressed in percent by weight, were:

| | <u>A</u> | <u>B</u> |
|--|----------|----------|
| Urethane resin (Texthane 620-C) | 29.7 | 29.7 |
| Urethane resin (Texthane 420-C) | 25.4 | 25.4 |
| Nonionic surfactant (Pluronic L-35) | 2.0 | 2.0 |
| Acrylic acid thickener (Carbopol 941 2% in DMF) | 6.0 | - |
| DMF | 36.9 | 42.9 |

Total solids of coating solution A was 17.9%. Coating solutions A and B were applied to a textured polyester taffeta by knife over roll coating, washed, dried and treated with a fluorocarbon/silicone water repellent. The following results were obtained:

| | <u>A</u> | <u>B</u> |
|---|----------|----------|
| Viscosity (Pa's) | 27 | 2.75 |
| Moisture vapor transmission rate (g/m ² /24 hours) | 1,434 | 1,281 |
| Hydrostatic resistance (kPa) | 166 | 207 |
| Coating weight (g/m ²) | 19.0 | 19.7 |

Example 2

The following coating composition, expressed in percent by weight, was prepared:

| | |
|--|-------|
| Urethane resin (Texthane 620-C) | 47.8 |
| Nonionic surfactant (Pluronic F-68) | 3.8 |
| DME | 43.6 |
| Acrylic acid thickener (Carbopol 934 2% in DME) | 4.8 |
| Total Solids | 18.2% |

This formulation was applied to a textured

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polyester taffeta fabric in the manner of Example 1 and evaluated with the following result:

| | |
|--|-------|
| Viscosity (Pa·s) | 4.35 |
| Moisture vapor transmission rate (g/m ² /24 hours) | 1,533 |
| Hydrostatic resistance (kPa) | 138 |
| Coating weight (g/m ²) | 13.9 |

As a class, the acrylic acid resins provide reliable, easy-to-process, thickened DME/urethane coating compositions, with the requisite coating and penetration properties, and the ability to coagulate with the urethane resin or resin system when introduced into the water coagulation bath while maintaining the desired microporous structure. The resulting coating is not water sensitive in that it withstands multiple machine launderings.

Example 3 -- Antimicrobial Microporous Coatings

A coating mixture was prepared containing two urethane resins, a nonionic surfactant and other diluents according to the mixing instructions given above and having the following formulation:

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| | <u>amount (wt%)</u> |
|--|---------------------|
| Urethane resin (Texthane 620-C) | 29.7 |
| Urethane resin (Texthane 420-C) | 25.4 |
| Nonionic surfactant (Pluronic L-35) | 2.0 |
| DMF | 40.9 |
| Water | 2.0 |

Total solids was 19.8%. To this solution various amounts of the bioactive silyl quaternary ammonium compound were added ranging from none (sample H) and from 0.2% to 0.6% (samples A through F) calculated on the weight of the overall solution. Entrant, the final sample, included for comparative purposes, is believed to be as described in U.S. 4,429,000. In addition, an afterfinish of 0.4% of the bioactive silyl quaternary ammonium salt was applied to samples also containing the bioactive compound in the urethane coating (D,E,F) and to a sample with no bioactive compound in the finish (G). The solutions and finishes were coated onto a 100% polyester woven fabric. For purposes of comparison, two commercially available vapor-permeable, water-repellant fabrics, Entrant and CoreTex, were evaluated.

All samples were evaluated for bacterial reduction and mildew coverage measured according to Dow Corning Corporate Test Method 0923 and modified AATCC Test Method 30 procedures, respectively, and

the results were as follows:

| <u>Sample</u> | <u>%Bioactive</u> | | <u>%Bacterial Reduction</u> | | <u>%Mildew Coverage</u> | |
|---------------|-------------------|---------------|-----------------------------|--------------|-------------------------|------------|
| | <u>Coating</u> | <u>Finish</u> | <u>Original</u> | <u>10MW*</u> | <u>Original</u> | <u>MW*</u> |
| A | 0.2 | - | 58.8 | 0 | 30 | 30 |
| B | 0.4 | - | 62.7 | 1.6 | 10 | 20 |
| C | 0.6 | - | 97.4 | 100 | 0 | 10 |
| D | 0.2 | 0.4 | 100 | 0 | 10 | 10 |
| E | 0.4 | 0.4 | 100 | 4.7 | 10 | 10 |
| F | 0.6 | 0.4 | 99.9+ | 3.3 | 10 | 10 |
| G | - | 0.4 | 99.9 | 0 | 90 | 75 |
| H | - | - | 0 | | 90 | |
| Entrant | | | 0 | | 90 | |

*machine washings

The results show that the amount of bacterial reduction is quite high on the original (unlaundered) samples. After ten machine washings (MW), the amount of bacterial reduction is generally low, but bacterial growth is prevented. That is, the coated fabric has bacteriostatic properties. In sample F (0.6% of bioactive compound in the coating), there was 100% reduction of bacteria; that is, the sample had bacteriocidal properties. In general, the treatments also reduced the growth of mildew substantially in comparison with untreated fabric and Entrant.

Example 4 -- Ultraviolet Light-Protected Coatings

A coating mixture was prepared containing two urethane resins, a nonionic surfactant, an ultraviolet light stabilizer and other diluents according to the mixing instructions given above and having the following formulation:

| | <u>amount (wt%)</u> |
|------------------------------|---------------------|
| Urethane resin | |
| (Textthane 620-C) | 29.7 |
| Urethane resin | |
| (Textthane 420-C) | 25.4 |
| Nonionic surfactant | |
| (Pluronic L-35) | 2.0 |
| Ultraviolet light stabilizer | |
| (Tinuvin® 292) | 0.4 |
| DMF | 40.9 |
| Water | 2.0 |

The solution was coated onto a 100% polyester woven fabric and coagulated using the wet coagulation process, then rinsed to remove any remaining DMF, and then dried.

The resulting coated fabric was exposed for 20 hours in a Fade-Ometer according to AATCC Test Method 16A-1982 to assess the level of protection afforded by the ultraviolet stabilizer. No appreciable change in color was observed after 20 hours, indicating that the fabric achieved the level of protection required by the marketplace for apparel end uses.

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Example 5 -- Flame Resistant Microporous Coatings

A treating bath was prepared by mixing 23.5 parts of Texthane 420C, 29.5 parts of Texthane 620C, 4 parts of Pluronic L-35, 21 parts of dimethylformamide (DMF), 15 parts of hexabromocyclododecane, and 7 parts of antimony trioxide, all parts being by weight in the same manner as in the previous examples. All of the ingredients formed a homogeneous solution except for the antimony trioxide, which was in the form of a suspension.

The above-described bath was coated onto a 100% polyester filament fabric, made of 2-ply 300/54 DuPont 56T continuous filament textured yarn. The weight of the fabric before coating was 271 g/m^2 . Coating was performed by a knife-over-roll method, after which the fabric passed into a bath containing 5% of DMF and 95% of water at 38°C to permit coagulation and replacement of the DMF with water. The DMF was then completely washed out of the fabric, after which the fabric was dried in a forced hot air oven. The coated fabric weighed 407 g/m^2 , and contained 7.1% of bromine, based on the weight of the coated fabric. When tested according to Federal Test Method 5903, the fabric had an afterflame time of 3.6 seconds, a char length of 14 cm, and no melt drip. In contrast, an untreated control showed extensive melt drip and burned its entire length. The coated fabric had a moisture vapor transmission (MVT) greater than $3500 \text{ g/m}^2/24$ hours and a Mullen hydrostatic pressure resistance of more than 55.2 kPa.

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Coated fabrics having a thin, microporous aromatic urethane coating have a moisture-vapor transmission of at least $800 \text{ g/m}^2/24$ hours and a hydrostatic pressure resistance of at least 69 kPa. Preferably, they are also resistant to degradation from ultraviolet light for at least 20 hours according to AATCC Test Method 16A-1982, or exhibit antimicrobial properties, or are significantly more resistant to flame than the corresponding untreated fabrics, or all of these.

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WHAT IS CLAIMED:

1. In a process of making a waterproof, water-vapor-permeable coated fabric having a microporous polyurethane layer thereon formed by the wet coagulation method, said process comprising applying a water-miscible, organic polar solvent solution of a polyurethane elastomer to a base fabric, immersing the thus-coated base fabric into an aqueous coagulation bath to extract the solvent from the polymer solution leaving a porous polyurethane matrix adhered to the base fabric, then washing and drying the coated fabric to produce a microporous, water-vapor-permeable polyurethane layer thereon, the improvement in which the polar organic solvent solution of polyurethane elastomer contains an acrylic acid thickener, the polyurethane elastomer coating, when applied to the base fabric, has a viscosity of at least 0.5 Pa.s, and the resulting microporous polyurethane layer has a moisture-vapor transmission rate of at least 800 grams/square meter/24 hours and a hydrostatic pressure resistance of at least 69 kPa.

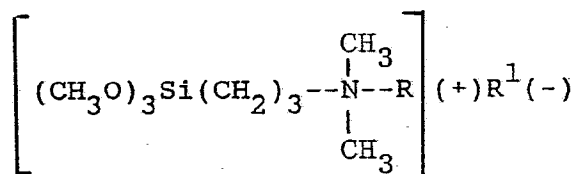
2. The process of claim 1 in which the polar organic solvent is dimethylformamide and the acrylic acid polymer thickener is soluble in dimethylformamide and has a molecular weight in the range of from about 1,000,000 to about 4,000,000.

3. The process of claim 2 in which a mixture of two acrylic acid polymers each having different molecular weights and both soluble in

dimethylformamide are used as the thickening agent.

4. A waterproof, water vapor-permeable coated fabric having a urethane coating with a moisture vapor transmission rate of at least $600 \text{ g/m}^2/24 \text{ hrs}$, and a hydrostatic pressure resistance of at least 69 kPa.

5. A process of making a waterproof, water-vapor-permeable, antimicrobial coated fabric having an antimicrobial, microporous polyurethane layer thereon formed by the wet coagulation method, said process comprising applying a water-miscible, polar organic solvent solution of a polyurethane elastomer to a base fabric, immersing the thus-coated base fabric into an aqueous coagulation bath to extract the solvent from the polymer solution leaving a porous polyurethane matrix adhered to the base fabric, then washing and drying the coated fabric, wherein the polyurethane elastomer solution contains from about 0.01 to about 10 weight percent of a bioactive silyl quaternary ammonium compound of the formula:



wherein R is an alkyl of 11 to 22 carbon atoms and R^1 is a bromine or chlorine.

6. The process of claim 5 in which from about 0.08 to about 4.0 weight percent of the bioactive compound is present in the solution.

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7. A waterproof, water-vapor-permeable antimicrobial coated fabric resistant to the spread of mildew, produced by the process of claim 5.

8. A urethane-coated fabric with durable antimicrobial properties, a moisture-vapor transmission of at least $800\text{g/m}^2/24$ hours, and a hydrostatic pressure resistance of at least 69 kPa.

9. A process of protecting a waterproof, water-vapor-permeable, coated fabric from ultraviolet light degradation, the coated fabric having a microporous polyurethane layer thereon formed by the wet coagulation method, said process comprising applying a water-miscible, polar organic solvent coating solution of an aromatic urethane elastomer to a base fabric, immersing the thus-coated base fabric into an aqueous coagulation bath to extract the solvent from the polymer solution leaving a porous aromatic urethane matrix adhered to the base fabric, then washing and drying the coated fabric, wherein the polyurethane elastomer solution contains an ultraviolet light protecting amount of hindered amine ultraviolet light stabilizer.

10. The process of claim 9 in which from about 0.1 to about 1.0 weight percent of the ultraviolet light stabilizer is present in the coating solution.

11. The process of claim 10 in which the amount of ultraviolet light stabilizer is in the range of from 0.1% to about 0.5%.

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12. The process of claim 9 in which the amount of the ultraviolet light stabilizer included in the coating solution provides effective protection against ultraviolet light for 20 hours in AATCC Test Method 16A-1982.

13. The process of claim 9 in which the ultraviolet light stabilizer is bis(1,2,2,6,6-pentamethyl-4-piperidinyl)sebacate.

14. A waterproof, water-vapor-permeable, ultraviolet light-resistant coated fabric produced by the process of claim 9.

15. A coated fabric having a thin, microporous aromatic urethane coating thereon resistant to degradation from ultraviolet light for at least 20 hours according to AATCC Test Method 16A-1982.

16. A coated fabric with a thin, microporous aromatic urethane coating thereon having a moisture-vapor transmission of at least $800\text{g/m}^2/24$ hours, a hydrostatic pressure resistance of at least 69 kPa and resistance to ultraviolet light for at least 20 hours according to AATCC Test Method 16A-1982.

17. A process of flame retardant treating a waterproof, water-vapor-permeable, coated fabric having a microporous polyurethane layer thereon formed by the wet coagulation method, said process comprising applying a water-miscible, polar organic solvent coating solution of an aromatic urethane

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elastomer to a base fabric, immersing the thus-coated base fabric into an aqueous coagulation bath to extract the solvent from the polymer solution leaving a porous aromatic urethane matrix adhered to the base fabric, then washing and drying the coated fabric, wherein the polyurethane elastomer solution contains a flame-retarding amount of a flame retardant.

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INTERNATIONAL SEARCH REPORT

International Application No PCT/US87/02278

| | | |
|---|--|--|
| I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ³ | | |
| According to International Patent Classification (IPC) or to both National Classification and IPC | | |
| INT Cl. 4 B32B 27/18; B32B 27/40 | | |
| US CL 427,246; 248/260,290,315.5,423.1,907 | | |
| II. FIELDS SEARCHED | | |
| Minimum Documentation Searched ⁴ | | |
| Classification System | Classification Symbols | |
| US | 427/245,246 428/260,290,315.5,315.7,315.9,423.1,904,907 | |
| Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁵ | | |
| | | |
| III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴ | | |
| Category [*] | Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷ | Relevant to Claim No. ¹⁸ |
| <u>Y</u> | US, A, 4,554,198 (VON BLUCHER) | <u>1-4,9-12</u> |
| X | 19 NOVEMBER 1985. ENTIRE COLUMNS 2 AND 3. | 17 |
| Y | US, A, 3,968,292 (PEARMAN) 06 JULY 1976 COLUMN 19, LINES 2-8 | 1-4,9-12 |
| <u>Y</u> | US, A, 4,507,413 (THOMA) 26 MARCH 1985 | <u>1-4,9-12</u> |
| X | COLUMN 2, LINES 63-68, ENTIRE COLUMN 7; CLAIMS 1 AND 10. | 14,15,16 |
| A | US, A, 4,504,541 (YASUDA) 12 MARCH 1985 | 5,6,7,8,13 |
| <p>[*] Special categories of cited documents: ¹⁵</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> | | |
| IV. CERTIFICATION | | |
| Date of the Actual Completion of the International Search ² | | Date of Mailing of this International Search Report ¹ |
| 02 DECEMBER 1987 | | 05 JAN 1988 |
| International Searching Authority ¹ | | Signature of Authorized Officer ¹⁰ |
| ISA/US | | W.J. VAN BALEN |